on γ_a/γ_b. Assuming collisions in the upper state only destroys the fit by interchanging a and b. Hence we assume collisions in the lower state ($2p_4$) only. A good fit with a-state scattering only is obtained if γ_a/γ_b is adjusted.

A serious difficulty in our treatment is the expansion in $\mathcal{I}$. For $\mathcal{N}=1.2$ (used in Ref. 4) we estimate an error of 15% near the Lamb dip. A more elaborate fit to Eq. (8) can be obtained numerically, but the agreement of Fig. 1 seems too good to be entirely fortuitous.

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[1] P. R. Berman and W. E. Lamb, Jr., Phys. Rev. A 2, 2435 (1970), and to be published.

[2] S. Stenholm, Phys. Rev. A 2, 2089 (1970).

[3] This assumption is justified at the end of the paper.

[4] R. H. Cordover and P. A. Bonczyk, Phys. Rev. 188, 696 (1969).

[5] B. L. Gyorffy, M. Borenstein, and W. E. Lamb, Jr., Phys. Rev. 169, 340 (1968).

[6] G. E. Notkin, S. G. Rautian, and A. A. Feoktistov, Zh. Eksp. Teor. Fiz. 52, 1673 (1967) [Sov. Phys. JETP 24, 788 (1967)].

[7] This is seen in the results of Ref. 2.

[8] The atomic injection density Λ_α is equal to the injection probability λ_α times the atomic density n_0.

[9] H. M. Foley, Phys. Rev. 69, 616 (1946).

[10] W. R. Bennett, Jr., and P. J. Kindlmann, Phys. Rev. 149, 38 (1966).

New Technique for the Measurement of NMR Splittings to Very High Accuracy

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A new technique for the measurement of frequency differences in NMR spectra to very high accuracy is presented. The technique has been used to measure frequency differences to a relative accuracy of 0.2 mHz and an estimated absolute accuracy of <1.0 mHz.

By conventional methods, splittings and shifts in high-resolution NMR spectra can be measured with an accuracy of ~0.1 Hz. While this is adequate for a wide variety of experiments, there are many areas of interest in NMR where there is a definite need for higher accuracy. Two of these areas that have received considerable attention recently are the density dependence of the chemical shift[1] and electric-field–induced effects.[2] Several specialized methods capable of higher absolute accuracy have been developed over the past few years and used to measure splittings and shifts. These include sideband techniques[3] with an accuracy of 0.05-0.1 Hz, spin-echo techniques[4] with an accuracy of 0.01 Hz, and a novel double-resonance technique[5] with an accuracy of 0.02 Hz.

In the present Letter, we wish to report the development of a new instrument—the nuclear double-sideband oscillator (NDSO)—for the measurement of frequency differences in NMR spectra to even higher accuracy. It has been demonstrated in the current work that the NDSO is capable of measuring (1) the absolute values of such differences to within an error of less than 1.0 mHz and (2) relative changes in these differences to within an error of less than 0.2 mHz. The NDSO has been used to determine that the scalar spin-spin coupling constant J in liquid CH_3F at 38.5°C is 43.3510 ± 0.0017 Hz. While the proton spectrum of liquid CH_3F is particularly well suited to the NDSO technique, the methods developed can be applied, with modifications, to the measurement of a wide variety of resonance spectra.

In order to introduce the concepts and define the notation to be used in treating the NDSO, we shall first discuss briefly the ordinary nuclear sideband oscillator,[6] a device which is commonly used in high-resolution NMR spectrometers[7] to stabilize the field-to-frequency ratio. As is shown in Fig. 1, the sample is placed in an rf coil forming the inductance of a parallel resonance circuit and is subjected to three different magnetic fields: (1) the static field $\vec{H}_0$; (2) the rf field $H_1 \cos\omega_0 t$, which oscillates in a direction perpendicular to $\vec{H}_0$ at radiofrequency ω_0; and (3) a modulation field $H_m \cos\omega_m t$, which oscillates in a direction parallel to $\vec{H}_0$ at an audiofrequency ω_m. Typically, when operating at a proton reso-

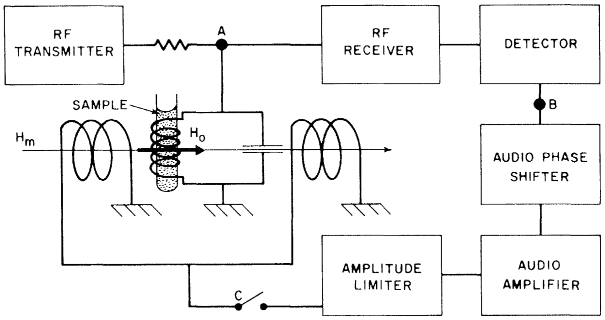

FIG. 1. Block diagram of the nuclear sideband oscillator.

nance, $H_0 \approx 14$ kG, $H_1 \approx 1$ mG, $H_m \approx 0.25$ G, $\omega_0/2\pi \approx 60$ MHz, and $\omega_m/2\pi \approx 5$ kHz. The sample is assumed here to have a spectrum which consists of a single line at frequency ω_R.

We first consider the circuit in Fig. 1 as an amplifier with the switch at C opened and with H_m generated by an external source. Because of H_m, the voltage $\mathfrak{v}_A$ observed at A is amplitude modulated when the nuclei are at or near resonance. After amplification and detection, an af signal $\mathfrak{v}_B$ is produced at B. If certain simple conditions are satisfied,[8] $\mathfrak{v}_B$ will contain at frequencies $\mu\omega_m$ a series of discrete components

$$\mathfrak{v}_B(\mu) = V_B(\mu)\cos[\mu\omega_m t + \varphi(\mu)],$$
$$\mu = 1, 2, \cdots, \infty. \tag{1}$$

The component amplitude $V_B(\mu)$ displays resonance behavior as a function of ω_0 whenever[9]

$$n\omega_m + \omega_R - \omega_0 = 0, \quad n = 0, \pm1, \pm2, \cdots. \tag{2}$$

In general, the dependence of $V_B(\mu)$ on ω_0 in the region of the centerband ($n=0$) or one of the sideband resonances ($n = 1, 2, \cdots$) will contain both absorption and dispersion terms.

The $n=1$ sideband of the frequency component $\mathfrak{v}_B(\mu=1)$ is of particular interest here. The frequency of $\mathfrak{v}_B(1)$ equals that of the modulation field and its amplitude $V_B(1)$ is a maximum when the modulation frequency equals $\omega_T \equiv \omega_0 - \omega_R$. Thus, if $\mathfrak{v}_B(1)$ is suitably shifted in phase and amplified, it can be used to drive the modulation coils. The switch at C in Fig. 1 is closed and an oscillator is formed.

In the absence of pulling effects from the circuit, the oscillation frequency is $\tilde{\omega} = \omega_T$, the frequency where $V_B(1)$ is a maximum. In general, however,

$$\tilde{\omega} = \omega_T + \epsilon(\theta), \tag{3}$$

where ϵ is the "instrumental shift" and θ is the phase shift due to the circuit at frequency $\tilde{\omega}$. When the phase shift θ_T at frequency ω_T vanishes, then $\epsilon = 0$. Typically there is sufficient gain in the loop for stable oscillation whenever ϵ is less than the linewidth. When oscillations occur, the limiter circuit will hold H_m at a constant value regardless of the magnitude of $V_B(1)$.

Let us now turn to the NDSO. In this case, the sample's NMR spectrum is assumed to consist of two lines, a and b, of equal intensity which occur at frequencies $\omega_R{}^a$ and $\omega_R{}^b$, respectively, with separation $\Delta \equiv \omega_R{}^a - \omega_R{}^b$. When such a sample is placed in the "ordinary" nuclear sideband oscillator shown in Fig. 1, then the possibility exists that the circuit will oscillate simultaneously on both lines. In fact, when the instrument parameters are suitably adjusted, two such simultaneous oscillations do occur with equal intensity at frequencies ω_a and ω_b, and a 100% modulated signal is observed at B. The observed beat frequency $\tilde{\Delta} \equiv \tilde{\omega}_a - \tilde{\omega}_b$ can be extremely stable; a reproducibility to within 0.2 mHz is typically obtained. This, then, is a nuclear double-sideband oscillator.

If ϵ_a and ϵ_b are the instrumental shifts for the two lines, then

$$\tilde{\Delta} = \Delta + (\epsilon_a - \epsilon_b). \tag{4}$$

The differential shift $\delta_{ab} \equiv \epsilon_a - \epsilon_b$ in general is not zero, and we are faced with the problem of eliminating or determining this shift. It is in this problem that much of the theoretical and experimental difficulty associated with the NDSO lies.

In order to illustrate how the elimination of δ_{ab} is carried out, we assume that the circuit phase shift $\theta_T{}^b$ at frequency $\omega_T{}^b$ is adjusted to zero with the phase shifter, so that $\epsilon_b = 0$. If we make certain simple assumptions which are satisfied in the present experiment, then

$$\delta_{ab} = \Delta(d\theta/d\tilde{\omega})g(\theta_b). \tag{5}$$

Here g is a function which depends only on the NMR line shape and width. If this shape were exactly Lorentzian, then the function g could be calculated. However, this assumption is not made since many high-resolution spectra are broadened by field inhomogeneities. In Eq. (5), $d\theta/d\tilde{\omega}$ is the derivative of the circuit phase shift with respect to frequency evaluated at $\tilde{\omega}_b$. Because this derivative contains contributions from both the rf and af portions of the circuit, its absolute value cannot be easily determined to the desired accuracy.

Fortunately, $d\theta/d\tilde{\omega}$ can be changed by known

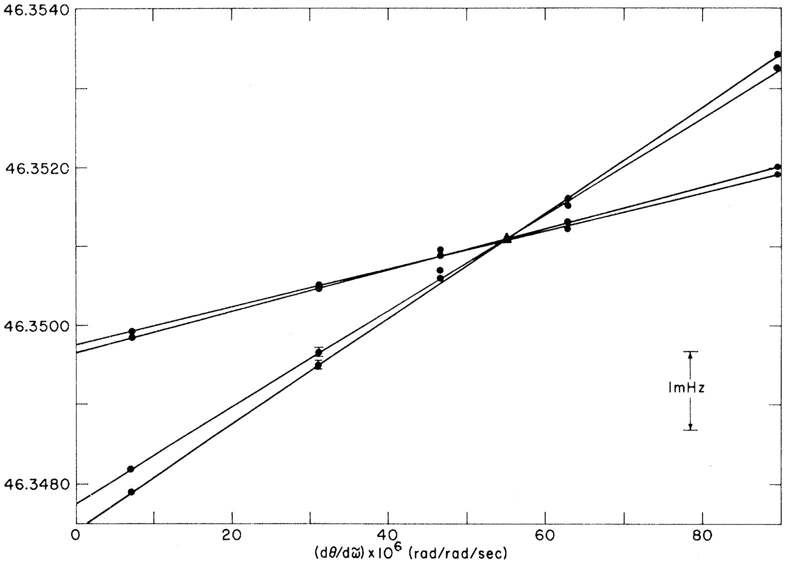

FIG. 2. Graph used to eliminate the differential instrumental shift δ_{ab}. At the intersection point labeled with the triangle, δ_{ab} vanishes. Each of the four sets of data was taken at a different field homogeneity. The intersection point and the slopes of the four straight lines were determined by a least-squares procedure.

increments by simple circuit adjustments. Furthermore, for a line broadened by field inhomogeneities as is the case here, $g(\theta_b)$ can be varied by the homogeneity controls. [We do not need to measure the changes in $g(\theta_b)$ quantitatively for this purpose.] What is done, then, is to fix $g(\theta_b)$ and measure $\tilde{\Delta}$ as a function of changes made in $d\theta/d\tilde{\omega}$. A straight line results with slope equal to $\Delta g(\theta_b)$. Subsequently $g(\theta_b)$ is changed, and a second straight line results. At the intersection of the two lines, $d\theta/d\tilde{\omega}=0$ and $\tilde{\Delta}=\Delta$.

In Fig. 2, four such straight lines taken for the proton spectrum of liquid CH_3F are shown. All the intersection points occur at the same value of $\tilde{\Delta}$ to within 0.2 mHz, and, moreover, the scatter is found to be consistent with the assumption that it is produced by random error in the data.

This analysis can be checked by verifying that Δ is independent of the NMR line shape and width when $d\theta/d\tilde{\omega}=0$. The amount by which a line broadened by field inhomogeneities has changed in shape and width can be monitored roughly by the signal intensity I (which can be taken to be the af voltage at B). In Fig. 3, a plot of $\tilde{\Delta}$ against I is shown for a case where $d\theta/d\tilde{\omega}\approx 0$. When I

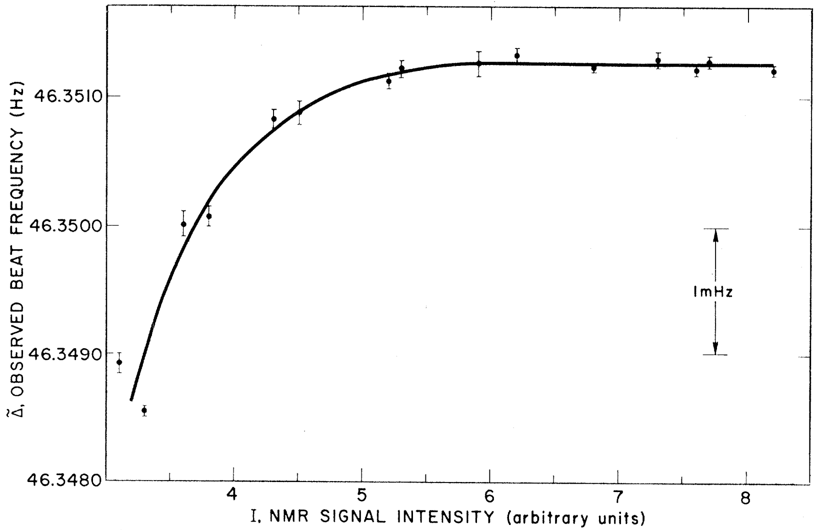

FIG. 3. The dependence of $\tilde{\Delta}$ on the field inhomogeneities. The NMR signal intensity is used as a measure of the linewidth.

is decreased by 40% below its maximum value, $\tilde{\Delta}$ changes by less than 0.2 mHz, indicating that the asymptotic value of Δ is $|\omega_T{}^a - \omega_T{}^b|$ to within an error of this order or less. When I is decreased by another 20%, $\tilde{\Delta}$ changes by 2 mHz. This relatively large change is caused by the fact that in this region the absorption line shape becomes highly distorted and asymmetric, and some of the approximations used in deriving Eq. (5) break down.

In the present case of CH_3F, we would like to set the magnitude of the scalar spin-spin coupling constant J equal to $|\omega_a - \omega_b|$. However, there are various mechanisms which produce "model shifts" (as distinct from the "instrumental shifts" δ_{ab} discussed above). As the name implies, such shifts result from the fact that our model is not exact. These shifts are of two types: (1) those associated with the approximations in the modulation theory and (2) those associated with effects that actually disturb the nuclear-spin energy levels (such as the Bloch-Siegert effect[10]). Each of these model shifts has been experimentally shown to be <0.3 mHz for the conditions used here.

The experimental equipment used in the current work is a modified Varian model A60 spectrometer. Only the original magnet, magnet controls, rf probe, and receiver were used. An ND100M Rohde and Schwarz frequency synthesizer was used as the transmitter. The phase shifter, limiter, and modulation field drive were specially constructed to meet the requirements of the NDSO. The beat frequency was determined by detecting the af signal at B, narrow banding the detected voltage, and measuring the frequency of the output with a counter operating in the period mode.

At optimum homogeneity, the full linewidth at half-height is ~0.5 Hz. It is at this homogeneity, of course, that the beat frequency is most stable. The time taken for 1000 periods of the beat note for CH_3F is ≈20 sec. If this frequency is measured ten times with the counter in the period mode, the typical standard deviation is ~30 μHz. The reason for this high stability lies in the fact that many of the fluctuations in such experimental conditions such as H_0 and the field homogeneity affect both lines by almost equal amounts, and only a very small residual differential effect remains.

The temperature T is stable to better than 0.1°K over times of the order of minutes, but drifts in T of ≈0.3°K do occur over times of the order of hours. Since $|dJ/dT| > 1$ mHz/°K,[11] both short-term fluctuations and long-term drifts are important. The absolute temperature in the probe was measured by a substitution technique[12] to better than 0.5°K.

The accuracy of the measurement of a relative change in Δ is limited at present by long-term instrumental drifts to ~0.2 mHz. The accuracy of an absolute measurement of Δ is limited at present to ~1 mHz by (1) the 0.2-mHz uncertainty in locating the crossing point in Fig. 2; (2) the upper limit of 0.6 mHz which can be put on the sum of the various "model shifts" discussed above; and (3) small systematic effects which are estimated to be less than 0.2 mHz. The error in our final result that $J = 46.3510 \pm 0.0017$ Hz at 38.5°C includes an additional contribution of 0.7 mHz from the uncertainty in the temperature measurement.

The present apparatus is limited to the study of systems with two lines of approximately equal intensity, and so is ideally suited to the proton spectrum of CH_3F. However, by using a split sample tube, one could equally well study the chemical shift of, for example, CF_4 relative to SF_6. Simple modifications of the present instrument would allow the study of multiline spectra. Furthermore, the use of a magnet with a higher homogeneity would lead to higher accuracy in the frequency measurements.

The nuclear double-sideband oscillator opens up the possibility of many new experiments. Apart from the obvious applications of determining a number of physical parameters to much higher accuracy, it offers the opportunity to measure very small changes in NMR frequencies, changes which might be produced by varying the temperature or density or by applying an external electric field. Work is underway at present to develop some of these applications. A full description of the NDSO including a complete analysis of the various pulling effects and a discussion of the instrumental details will be published elsewhere.

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[1] S. Mohanty and H. J. Bernstein, Chem. Phys. Lett. 4, 575 (1970); A. K. Jameson, C. J. Jameson, and H. S. Gutowsky, J. Chem. Phys. 53, 2310 (1970).

[2] C. W. Hilbers and C. MacLean, Mol. Phys. 16, 275 (1969).

[3] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, *High Resolution NMR Spectroscopy* (Pergamon, Oxford, England, 1965), Vol. 1.

[4] J. G. Powles and J. H. Strange, Discuss. Farad. Soc. 34, 30 (1962); D. K. Green, A. Hartland, and H. Y. Carr, Bull. Amer. Phys. Soc. 11, 311 (1966).

[5] R. Freeman and B. Gestblom, J. Chem. Phys. 48, 5008 (1968).

[6] W. A. Anderson, Rev. Sci. Instrum. 33, 1160 (1962).

[7] Analytical Instruments Division, Instruction Manual No. 87-102-300 (Varian Associates, Palo Alto, Calif., 1964), Revision E, p. 2.

[8] O. Haworth and R. E. Richards, in *Progress in N. M. R. Spectroscopy*, edited by S. W. Emsley, J. Feeney, and L. H. Sutcliff (Pergamon, New York, 1966), Vol. 1, p. 1.

[9] All frequencies are defined to be positive.

[10] F. Bloch and A. Siegert, Phys. Rev. 57, 522 (1940).

[11] A precise determination of dJ/dT will be published elsewhere.

[12] A. L. Van Geet, Anal. Chem. 42, 679 (1970).

Motion of Ions at Finite Velocities in Helium II†

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The drag force on an ion moving through liquid helium II at finite velocities is discussed in terms of localized roton states near the ion. These ideas are compared with experiments on positive and negative ions below 1°K.

The relationship between the drift velocity v_i and the electric field E for positive and negative ions in helium II, up to the nucleation velocity, resembles the curves shown in Figs. 1 and 2. The ion mobility μ, which should strictly be defined from $1/\mu = (\partial E/\partial v_i)_{v_i=0}$, was first discussed and related to experiment by Reif and Meyer on the basis of kinetic-theory arguments.[1] More sophisticated theory[2] and experiments[3] have produced a quite satisfactory account of ion mobilities. The motion at finite velocities, however, has remained less well understood and our purpose is to advance a hypothesis to account for the

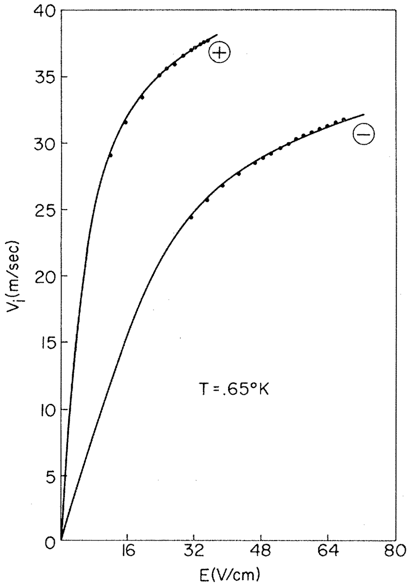

FIG. 1. The average drift velocity of positive and negative ions at $T=0.65$°K. The points are experimental data. The curves result from Eq. (8) using the fitted constants $f_+=0.065$, $\mu=400$ cm^2/V sec, $f_-=0.010$, and $\mu=65$ cm^2/V sec.

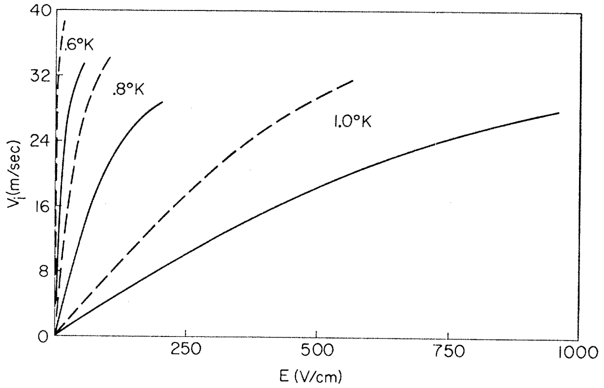

FIG. 2. The drift velocity of positive (dashed lines) and negative (solid lines) ions at $T=0.6$, 0.8, and 1.0°K. The curves result from Eq. (8) using mobility data of Ref. 1 and the constants $f_+=0.060$, $f_-=0.012$.